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Rubidium and Cesium Selenocarboxylates: Synthesis and Characterization

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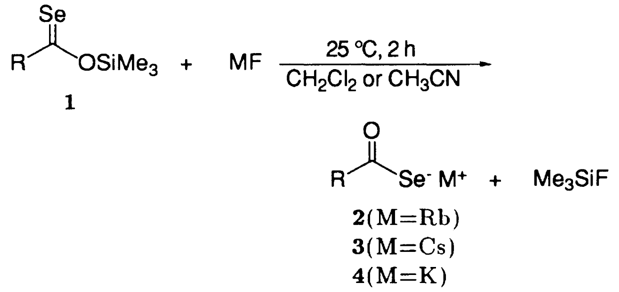
Rubidium and cesium selenocarboxylates (**2** and **3**) were found to be synthesized in good to high yields from the reaction of *O*-trimethylsilyl selenocarboxylates with rubidium and cesium fluorides. The spectroscopic properties of **2** and **3** are also given.

The chemistry of selenocarboxylic acid derivatives has been the subject of considerable research in recent decades. Most of them have focused on the synthetic utility of selenocarboxylic acid esters.[1] In contrast, selenocarboxylic acid metal salts have little been studied in spite of their synthetic importance. We have recently established the preparation of lithium,[2] sodium,[3] and potassium[4,5] selenocarboxylates, which can be prepared by the direct reaction of acyl chlorides with the corresponding metal selenides in hexane or ether[2,3] or by the reaction of diacyl selenides with potassium hydroxide in methanol[4] or with potassium methoxide in ether/hexane.[5] However, these methodologies could not be applied to the synthesis of selenocarboxylic acid heavy alkali metal salts because the starting material, M_2Se or MOH (M=Rb, Cs), was not accessible. In the course of our studies on the synthesis of new chalcogenocarboxylic acid derivatives, a series of *O*-triorganosilyl selenocarboxylates **1** have been prepared[6] and used as an effective selenocarboxylating agent.[7] Very recently, we have succeeded in the isolation of rubidium and cesium selenocarboxylates from *O*-trimethylsilyl selenocarboxylates and the corresponding metal fluorides.[8] In this paper the full details of their synthesis and characterization are described.

Results and Discussion

When rubidium fluoride and an equal amount of *O*-trimethylsilyl selenoester (**1c**) were stirred in dichloromethane at room temperature, the purple color of the ester gradually disappeared, with yellow precipitates. After this was stirred for 1.5 h, then collection of the precipitates by filtration and recrystallization from a mixed solvent of methanol and ethanol (1 : 2) below −20 °C afforded 74% rubidium benzenecarboselenoate (**2c**) as yellow plate crystals. Similarly, the reaction of a variety of *O*-silyl selenoesters **1a**, **1b**, **1d—i** with rubidium fluoride yielded the corresponding aliphatic and aromatic rubidium selenocarboxylates **2a**, **2b**, **2d—i** in 60—90% isolated yields (Eq. 1, Table 1). Under the same conditions, the reaction with cesium fluoride instead of rubidium fluoride afforded almost quantitative yields of cesium salts **3a—i**. Rubidium (**2a**) and cesium selenoacetates (**3a**) were obtained by using acetonitrile as a solvent. The structures of **2** and **3** were confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectra (Table 1) and elemental analysis or by conversion into *Se*-alkyl esters. It is noted that the reaction with other rubidium and cesium halides such as RbCl, RbBr, RbI, etc. did not occur under various conditions even with reflux in tetrahydrofuran and acetonitrile. Thus, the high affinity of silicon for fluorine may be the driving force to cleave oxygen–silicon bond in **1**.[9] In addition, the reaction of **1** with lithium, sodium, and potassium fluorides under various conditions was done. Although the reactions with the former two did not take place, the reaction with potassium fluoride gradually proceeded to give the expected potassium selenocarboxylate (**4e**) in 45% yield (Eq. 1).



1

2(M=Rb)
3(M=Cs)
4(M=K)

(1)

The obtained rubidium **2** and cesium **3** salts are white (R=alkyl) or yellow plate or needle crystals (R=aryl). The metal salts **2** and **3** decomposed at room temperature with liberation of red selenium upon exposure to the air. Under an inert atmosphere at −20 °C, however, aromatic derivatives are relatively stable, and no appreciable change is observed at least for a week.[10] The aliphatic derivatives are less stable. In particular, acetyl derivatives **2a** and **3a** are highly unstable and quickly decompose even below −20 °C under an argon atmosphere.[11]

The carbonyl stretching frequencies, ^{13}C and ^{77}Se NMR spectra of the COSe moiety of **2** and **3** are collected in Table 1. The C=O stretch appeared in the region of 1520—1560 cm^{-1}, which was lower than those of the corresponding *Se*-alkyl esters by 100—130 cm^{-1}.[3] In ^{13}C NMR spectra, the C=O signals were observed in the region of δ=210—220 regardless of the substituents attached to the C=O group. On the other hand, ortho-

Table 1. Yields and Spectral Data of Rubidium **2** and Cesium Selenocarboxylates **3**

	$RCOSe^- M^+$		Yield[a)]	Mp[b)]	IR (cm^{-1})[c)]	^{13}C NMR[d)]	^{77}Se NMR[e)]
	R	M	%	°C	ν C=O	δ C=O	δ
2a	CH_3	Rb	74	—	1538[f)]	219.7	—
2b	t-C_4H_9	Rb	71	86—108	1560	228.7	—
2c	C_6H_5	Rb	74	141—159	1545	215.8	370.8
2d	2-$CH_3C_6H_4$	Rb	74	88—112	1543	221.0	474.1
2e	4-$CH_3C_6H_4$	Rb	80	143—167	1546	215.1	357.3
2f	2-$CH_3OC_6H_4$	Rb	80	111—119	1539	220.8	475.7
2g	4-$CH_3OC_6H_4$	Rb	75	101—123	1542	213.8	339.8
2h	2-ClC_6H_4	Rb	82	128—142	1519	216.9	505.5
2i	4-ClC_6H_4	Rb	69	186—208	1543	214.0	377.9
3a	CH_3	Cs	65	—	1539[f)]	219.9	—
3b	t-C_4H_9	Cs	74	95—104	1558	230.1	—
3c	C_6H_5	Cs	79	173—198	1547	215.7	388.7
3d	2-$CH_3C_6H_4$	Cs	70	110—122	1556	220.7	494.2
3e	4-$CH_3C_6H_4$	Cs	80	138—145	1547	215.2	361.9
3f	2-$CH_3OC_6H_4$	Cs	80	110—120	1557	220.8	490.3
3g	4-$CH_3OC_6H_4$	Cs	68	151—158	1538	213.8	350.9
3h	2-ClC_6H_4	Cs	81	155—170	1524	216.8	517.1
3i	4-ClC_6H_4	Cs	76	151—176	1546	213.8	385.9

a) Isolated yield. b) Decomposition. c) KBr. d) CD_3OD. e) CD_3OD, Standard: $(CH_3)_2Se$. f) Nujol.

substituted aromatic derivatives showed the lower field shift in ^{77}Se NMR spectra by about 115—140 ppm. This is characteristic of **2** and **3** since no critical difference was obtained for ^{77}Se NMR spectra of *Se*-alkyl esters.[12)]

The $\nu_{C=O}$ band, $^{13}C=O$, and ^{77}Se signals of a series of alkali metal salts in Table 2 indicated that the spectral properties of the COSe moiety does not vary much with the counter metal cation. This has suggested that a series of alkali metal salts bear a structural resemblance to each other with respect to the degree of the localization of the electron in the selenocarboxylic group.[13)]

Experimental

General. The melting points were obtained using a Yanagimoto micro-melting point apparatus and were uncorrected. The IR spectra were measured on a JASCO grating IR spectrometer IR-G and a Perkin–Elmer FT-IR 1640. The ^1H NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) with tetramethylsilane as an internal standard, and the following abbreviations were used; s: singlet, m: multiplet. The ^{13}C NMR spectra were obtained from a JEOL JNM-GX-270 (67.8 MHz). The ^{77}Se NMR spectra were recorded on a JEOL JNM-GX-270 (51.5 MHz) with dimethyl selenide as an external standard. Elemental analyses were done at the Elemental Analyses Center of Kyoto University.

Materials. Selenium (powder), sodium metal, rubidium fluoride, chloride, bromide, and iodide, cesium fluoride, chloride, bromide, and iodide, lithium, sodium and potassium fluorides were commercial grade and used without further purification. Trimethylsilyl chloride, acetyl, pivaloyl, and benzoyl chlorides were commercial grade and distilled before use. Other acyl chlorides (2-methyl-, 4-methyl-, 2-methoxy-, 4-methoxy-, 2-chloro-, and 4-chloro-benzoyl chlorides)[14)] and *O*-trimethylsilyl selenocarboxylates[6)] were prepared as described in the literature. Dichloromethane was distilled from phosphorus pentoxide and degassed. Methanol and ethanol were distilled from magnesium powder and degassed. Ether and tetrahydrofuran (THF) were distilled from sodium diphenylketyl and degassed. All manipulations were done under argon.

The preparation of **2b**, **2c**, **3b**, and **3c** are described in detail as typical procedures for aliphatic and aromatic rubidium **2** and cesium salts **3**, respectively.

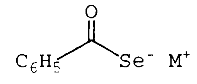
Rubidium Selenoacetate (2a): Similarly to **2b**, the reaction of *O*-trimethylsilyl selenoacetate (**1a**) (0.414 g, 2.12 mmol) with rubidium fluoride (0.221 g, 2.12 mmol) in acetonitrile (5 mL) gave 0.326 g (74%) of rubidium selenoacetate (**2a**) as white microcrystalline solids. The salts (**2a**) were converted into *Se*-propyl selenoacetate (90%). The IR spectrum was exactly consistent with that of the authentic sample.[5)]

(2a): IR (Nujol) 2922, 2842, 1538 (C=O), 1463, 1378, 1252, 1017, 917, 722, 648 cm^{-1}; ^1H NMR (CD_3OD) $\delta=2.50$ (s, CH_3); ^{13}C NMR (CD_3OD) $\delta=44.4$ (CH_3), 219.7 (C=O).

Rubidium 2,2-Dimethylpropaneselenoate (2b): To a solution of *O*-trimethylsilyl 2,2-dimethylpropaneselenoate (**1b**) (0.309 g, 1.30 mmol) in dichloromethane (5 mL), rubidium fluoride (0.125 g, 1.30 mmol) was added, and the mixture was stirred at 25 °C for 2 h. The solution turned pale yellow from orange. Collection of the resulting precipitates by filtration, and washing with ether (1 mL) gave 0.214 g (71%) of rubidium 2,2-dimethylpropaneselenoate (**2b**) as white microcrystalline solids. The salt (**2b**, 0.249 g, 1.00 mmol) was stirred in methyl iodide at 25 °C for 2 h. Removal of the precipitates by filtration and vacuum distillation of the filtrate yielded 0.165 g (92%) of *Se*-methyl 2,2-dimethylpropaneselenoate (bp 70—72 °C/760 Torr, (1 Torr=133.322 Pa), lit,[5)] 70 °C/760 Torr). The IR spectrum was exactly consistent with that of the authentic sample.

(2b): Mp 86—108 °C (decomp); IR (KBr) 2958, 1610, 1577, 1560, (C=O), 1471, 1459, 1383, 1358, 1233, 1036, 932,

Table 2. Spectral Data of Alkali Metal Selenocarboxylates

 M	IR (cm^{-1})$^{a)}$ ν C=O	^{13}C NMR$^{b)}$ δ C=O	^{77}Se NMR$^{c)}$ δ	Ref.
Li	1556	217.5	371.1	2
Na	1525	216.1	361.6	3
K	1538	215.9	363.0	4
Rb	1545$^{d)}$	215.8	370.8	
Cs	1547$^{d)}$	215.7	388.7	

a) Nujol, b) CD_3OD, c) CD_3OD, Standard: $(CH_3)_2Se$, d) KBr.

805, 609 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=1.17$ (s,$(CH_3)_3C$); ^{13}C NMR (CD_3OD) $\delta=27.9$ ($(\underline{C}H_3)_3C$), 52.3 ($(CH_3)_3\underline{C}$), 228.7 (C=O).

Rubidium Benzenecarboselenoate (2c): To a solution of *O*-trimethylsilyl benzenecarboselenoate (**1c**) (0.283 g, 1.10 mmol) in dichloromethane (5 mL), rubidium fluoride (0.115 g, 1.10 mmol) was added, and the mixture was stirred at 25 °C for 2 h. The solution turned pale yellow from purple. Collection of the resulting precipitates by filtration, washing with ether (1 mL) and recrystallization from a mixed solvent (3 mL) of methanol and ethanol (1 : 2) at −20 °C for 1 h gave 0.219 g (74%) of rubidium benzenecarboselenoate (**2c**) as yellow needles. The salt (**2c**) was converted into *Se*-ethyl benzenecarboselenoate (88%). The IR spectrum was exactly consistent with that of the authentic sample.[3)]

(2c): Mp 141—159 °C (decomp); IR (KBr) 3056, 1577, 1545 (C=O), 1441, 1298, 1230, 1199, 1162, 1070, 1019, 905, 767, 691, 632, 490 cm^{-1}; ^{1} H NMR (CD_3OD) $\delta=7.30$—8.14 (m, Ar); ^{13}C NMR (CD_3OD) $\delta=128.2$, 129.2, 131.7, 147.8 (Ar), 215.8 (C=O) ^{77}Se NMR (CD_3OD) $\delta=370.8$. Found: C, 31.09; H, 1.99%. Calcd for C_7H_5ORbSe: C, 31.19; H, 1.87%.

Rubidium 2-Methylbenzenecarboselenoate (2d): Similarly to **2c**, the reaction of *O*-trimethylsilyl 2-methylbenzenecarboselenoate (**1d**) (0.270 g, 0.99 mmol) with rubidium fluoride (0.104 g, 0.99 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (5.5 mL) of ethanol and ether (1 : 10) gave 0.208 g (74%) of rubidium 2-methylbenzenecarboselenoate (**2d**) as yellow needles. The salt (**2d**) was converted into *Se*-methyl 2-methylbenzenecarboselenoate (85%). The IR spectrum was exactly consistent with that of the authentic sample.[3)]

(2d): Mp 88—112 °C (decomp); IR (KBr) 3059, 1560, 1543 (C=O), 1207, 1179, 1115, 904, 857, 762, 729, 671, 664 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=2.36$ (s, 3H, CH_3), 7.11—7.60 (m, 4H, Ar); ^{13}C NMR (CD_3OD) $\delta=19.9$ (CH_3), 125.6, 127.8, 128.7, 131.0, 131.8, 152.2 (Ar), 221.0 (C=O); ^{77}Se NMR (CD_3OD) $\delta=474.1$.

Rubidium 4-Methylbenzenecarboselenoate (2e): Similarly to **2c**, the reaction of *O*-trimethylsilyl 4-methylbenzenecarboselenoate (**1e**) (0.557 g, 2.13 mmol) with rubidium fluoride (0.222 g, 2.13 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (3 mL) of methanol and ethanol (1 : 2) gave 0.483 g (80%) of rubidium 4-methylbenzenecarboselenoate (**2e**) as yellow needles. The salt (**2e**) was converted into *Se*-methyl 4-methylbenzenecarboselenoate (93%). The IR spectrum was exactly consistent with that of the authentic sample.[3)]

(2e): Mp 143—167 °C (decomp); IR (KBr) 3050, 1606, 1579, 1546 (C=O), 1291, 1200, 1158, 1107, 1011, 903, 820, 789, 762, 717, 628, 615, 470, 454 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=2.31$ (s, 3H, CH_3), 7.09—8.06 (m, 4H, Ar); ^{13}C NMR (CD_3OD) $\delta=21.4$ (CH_3), 128.9, 129.5, 142.3, 145.2 (Ar), 215.1 (C=O); ^{77}Se NMR (CD_3OD) $\delta=357.3$.

Rubidium 2-Methoxybenzenecarboselenoate (2f): Similarly to **2c** the reaction of *O*-trimethylsilyl 2-methoxybenzenecarboselenoate (**1f**) (0.417 g, 1.45 mmol) with rubidium fluoride (0.151 g, 1.45 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (5.5 mL) of ethanol and ether (1 : 10) gave 0.350 g (80%) of rubidium 2-methoxybenzenecarboselenoate (**2f**) as yellow needles: Mp 111—119 °C (decomp); IR (KBr) 2954, 1560, 1539 (C=O), 1187, 904, 858, 762, 662 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=2.36$ (s, 3H, CH_3O), 7.12—7.61 (m, 4H, Ar); ^{13}C NMR (CD_3OD) $\delta=20.0$ (CH_3O), 125.8, 127.9, 128.8, 131.2, 132.0, 152.3 (Ar), 220.8 (C=O); ^{77}Se NMR (CD_3OD) $\delta=475.7$. Found; C, 32.34; H, 2.36%. Calcd for $C_8H_7O_2RbSe$: C, 32.08; H, 2.36%.

Rubidium 4-Methoxybenzenecarboselenoate (2g): Similarly to **2c**, the reaction of *O*-trimethylsilyl 4-methoxybenzenecarboselenoate (**1g**) (0.250 g, 0.87 mmol) with rubidium fluoride (0.091 g, 0.87 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (3 mL) of methanol and ethanol (1 : 5) gave 0.195 g (75%) of rubidium 4-methoxybenzenecarboselenoate (**2g**) as yellow needles. The salt (**2g**) was converted into *Se*-methyl 4-methoxybenzenecarboselenoate (85%). The IR spectrum was exactly consistent with that of the authentic sample.[3)]

(2g): Mp 101—123 °C (decomp); IR (KBr) 3074, 2964, 1603, 1583, 1542 (C=O), 1496, 1253, 1203, 1151, 1104, 1026, 906, 831, 784, 646, 619, 504, 455 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=3.80$ (s, 3H, CH_3O), 6.81—8.17 (m, 4H, Ar); ^{13}C NMR (CD_3OD) $\delta=55.8$ (CH_3O), 113.2, 131.5, 140.8, 163.5 (Ar), 213.8 (C=O); ^{77}Se NMR (CD_3OD) $\delta=339.8$.

Rubidium 2-Chlorobenzenecarboselenoate (2h): Similarly to **2c**, the reaction of *O*-trimethylsilyl 2-chlorobenzenecarboselenoate (**1h**) (0.405 g, 1.39 mmol) with rubidium fluoride (0.145 g, 1.39 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (7.2 mL) of methanol and ether (1 : 8) gave 0.349 g (82%) of rubidium 2-chlorobenzenecarboselenoate (**2h**) as yellow plates. The salt (**2h**) was converted into *Se*-ethyl 2-chlorobenzenecarboselenoate (84%). The IR spectrum was exactly consistent with that of the authentic sample.[3)]

(2h): Mp 128—142 °C (decomp); IR (KBr) 3037, 1519 (C=O), 1498, 1054, 1032, 918, 770, 736, 703, 638, 544 cm^{-1}; ^{1}H NMR (CD_3OD) δ=7.21—7.60 (m, Ar); ^{13}C NMR (CD_3OD) δ=127.0, 129.0, 129.6, 129.9, 130.3, 151.5 (Ar), 216.9 (C=O); ^{77}Se NMR (CD_3OD) δ=505.5.

Rubidium 4-Chlorobenzenecarboselenoate (2i): Similarly to **2c**, the reaction of *O*-trimethylsilyl 4-chlorobenzenecarboselenoate (**1i**) (0.351 g, 1.20 mmol) with rubidium fluoride (0.125 g, 1.20 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (3 mL) of methanol and ethanol (1 : 1) gave 0.251 g (69%) of rubidium 4-chlorobenzenecarboselenoate (**2i**) as yellow plates: Mp 186—208 °C (decomp); IR (KBr) 3056, 1576, 1543 (C=O), 1476, 1226, 1193, 1152, 1101, 1086, 1013, 903, 838, 719, 711, 630, 623, 557, 469 cm^{-1}; ^{1}H NMR (CD_3OD) δ=7.28—8.13 (m, Ar); ^{13}C NMR (CD_3OD) δ=128.2, 130.8, 137.8, 146.3 (Ar), 214.0 (C=O); ^{77}Se NMR (CD_3OD) δ=377.9. Found: C, 27.20; H, 1.45%. Calcd for $C_7H_4ClORbSe$: C, 27.66; H, 1.33%.

Cesium Selenoacetate (3a): Similarly to **3b**, the reaction of *O*-trimethylsilyl selenoacetate (**1a**) (0.431 g, 2.21 mmol) with cesium fluoride (0.335 g, 2.21 mmol) in acetonitrile (5 mL) gave 0.364 g (65%) of cesium selenoacetate (**3a**) as white microcrystalline solids. The salts (**3a**) was converted into *Se*-propyl selenoacetate (81%). The IR spectrum was exactly consistent with that of the authentic sample.$^{5)}$

(3a): IR (Nujol) 2952, 2856, 1539 (C=O), 1464, 1377, 1242, 1106, 962, 724, 605 cm^{-1}; ^{1}H NMR (CD_3OD) δ=2.47 (CH_3); ^{13}C NMR (CD_3OD) δ=44.4 (CH_3); 219.9 (C=O).

Cesium 2,2-Dimethylpropaneselenoate (3b): To a solution of *O*-trimethylsilyl 2,2-dimethylpropaneselenoate (**1b**) (0.406 g, 1.70 mmol) in dichloromethane (5 mL), cesium fluoride (0.258 g, 1.70 mmol) was added, and the mixture was stirred at 25 °C for 2 h. The solution turned pale yellow from orange. Collection of the resulting precipitates by filtration and washing with ether (1 mL) gave 0.335 g (74%) of cesium 2,2-dimethylpropaneselenoate (**3b**) as white microcrystalline solids. The salt (**3d**, 0.269 g, 1.00 mmol) was stirred in methyl iodide at 25 °C for 2 h. Removal of the precipitates by filtration and vacuum distillation of the filtrate yielded 0.168 g (94%) of *Se*-methyl 2,2-dimethylpropaneselenoate (Bp 70—72 °C/760 Torr, lit,$^{5)}$ 70 °C/760 Torr). The IR spectrum was exactly consistent with that of the authentic sample.$^{5)}$

(3b): Mp 95—104 °C (decomp); IR (KBr) 2966, 1615, 1558 (C=O), 1471, 1453, 1381, 1356, 1231, 1202, 1033, 928, 806, 603, 460 cm^{-1}; ^{1}H NMR (CD_3OD) δ=1.18 (s, $(CH_3)_3C$); ^{13}C NMR (CD_3OD) δ=29.7 ($(\underline{C}H_3)_3C$), 52.5 ($(CH_3)_3\underline{C}$), 230.1 (C=O).

Cesium Benzenecarboselenoate (3c): To a solution of *O*-trimethylsilyl benzenecarboselenoate (**1c**) (0.258 g, 1.00 mmol) in dichloromethane (5 mL), cesium fluoride (0.151 g, 1.00 mmol) was added, and the mixture was stirred at 25 °C for 2 h. The solution turned pale yellow from purple. Collection of the resulting precipitates by filtration, washing with ether (1 mL) and recrystallization from a mixed solvent (2 mL) of methanol and ethanol (1 : 1) at −20 °C for 1 h gave 0.250 g (79%) of cesium benzenecarboselenoate (**3c**) as yellow plates. The salt (**3c**) was converted into *Se*-ethyl benzenecarboselenoate (88%). The IR spectrum was exactly consistent with that of the authentic sample.$^{3)}$

(3c): Mp 173—198 °C (decomp); IR (KBr) 3050, 1585, 1547 (C=O), 1440, 1298, 1200, 1162, 1070, 1020, 900, 773, 692, 680, 633, 490 cm^{-1}; ^{1}H NMR (CD_3OD) δ=7.28—8.14 (m, Ar); ^{13}C NMR (CD_3OD) δ=128.3, 129.2, 131.8, 147.9 (Ar), 215.7 (C=O); ^{77}Se NMR (CD_3OD) δ=388.7. Found: C, 26.43; H, 1.72%. Calcd for C_7H_5CsOSe: C, 26.52; H, 1.59%.

Cesium 2-Methylbenzenecarboselenoate (3d): Similarly to **3c**, the reaction of *O*-trimethylsilyl 2-methylbenzenecarboselenoate (**1d**) (0.608 g, 2.24 mmol) with cesium fluoride (0.341 g, 2.24 mmol) in dichloromethane (5 mL) and recrystallization from ethanol (1.5 mL) gave 0.518 g (70%) of cesium 2-methylbenzenecarboselenoate (**3d**) as yellow plates. The salt (**3d**) was converted into *Se*-methyl 2-methylbenzenecarboselenoate (88%). The IR spectrum was exactly consistent with that of the authentic sample.$^{3)}$

(3d): Mp 110—122 °C (decomp); IR (KBr) 3000, 1605, 1575, 1556, (C=O), 1460, 1380, 1199, 1175, 1120, 902, 890, 870, 770, 762, 728, 677, 650, 640, 515, 492, 460 cm^{-1}; ^{1}H NMR (CD_3OD) δ=2.35 (s, 3H, CH_3), 7.10—7.52 (m, 4H, Ar); ^{13}C NMR (CD_3OD) δ=19.9 (CH_3), 125.8, 127.9, 128.8, 131.1, 132.0, 152.4 (Ar), 220.7 (C=O); ^{77}Se-NMR (CD_3OD) δ=494.2.

Cesium 4-Methylbenzenecarboselenoate (3e): Similarly to **3c**, the reaction of *O*-trimethylsilyl 4-methylbenzenecarboselenoate (**1e**) (0.535 g, 1.97 mmol) with cesium fluoride (0.299 g, 1.97 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (10 mL) of methanol and ethanol (1 : 1) gave 0.528 g (80%) of cesium 4-methylbenzenecarboselenoate (**3e**) as yellow plates: Mp 138—145 °C (decomp); IR (KBr) 3050, 1607, 1580, 1547 (C=O), 1295, 1260, 1200, 1161, 1110, 903, 824, 792, 632, 472 cm^{-1}; ^{1}H NMR (CD_3OD) δ=2.32 (s, 3H, CH_3), 7.10—8.03 (m, 4H, Ar); ^{13}C NMR (CD_3OD) δ=21.4 (CH_3), 128.8, 129.5, 142.1, 145.3 (Ar), 215.2 (C=O); ^{77}Se NMR (CD_3OD) δ=361.9. Found: C, 28.87; H, 2.12%. Calcd for C_8H_7CsOSe: C, 29.03; H, 2.13%.

Cesium 2-Methoxybenzenecarboselenoate (3f): Similarly to **3c**, the reaction of *O*-trimethylsilyl 2-methoxybenzenecarboselenoate (**1f**) (0.234 g, 0.81 mmol) with cesium fluoride (0.122 g, 0.81 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (4.5 mL) of ethanol and ether gave 0.225 g (80%) of cesium 2-methoxybenzenecarboselenoate (**3f**) as yellow needles. The salt (**3f**) was converted into *Se*-methyl 2-methoxybenzenecarboselenoate (90%). The IR spectrum was exactly consistent with that of the authentic sample.$^{3)}$

(3f): Mp 110—120 °C (decomp); IR (KBr) 2922, 1600, 1572, 1557 (C=O), 1539, 1172, 1111, 901, 761, 754, 722, 672, 644 cm^{-1}; ^{1}H NMR (CD_3OD) δ=2.36 (s, 3H, CH_3O), 7.09—7.58 (m, 4H, Ar); ^{13}C NMR (CD_3OD) δ=20.0 (CH_3O), 125.9, 127.9, 128.8, 131.3, 132.0, 152.5 (Ar), 220.8 (C=O); ^{77}Se NMR (CD_3OD) δ=490.3.

Cesium 4-Methoxybenzenecarboselenoate (3g): Similarly to **3c**, the reaction of *O*-trimethylsilyl 4-methoxybenzenecarboselenoate (**1g**) (0.438 g, 1.52 mmol) with cesium fluoride (0.231 g, 1.52 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (9 mL) of methanol and ethanol (1 : 5) gave 0.361 g (68%) of cesium 4-methoxybenzenecarboselenoate (**3g**) as yellow needles: Mp 151—158 °C (decomp); IR (KBr) 3100, 1602, 1580, 1538 (C=O), 1503, 1499, 1311, 1250, 1204, 1182, 1151, 1110, 1032, 904, 831, 791, 652, 630, 620, 505, 453 cm^{-1}; ^{1}H NMR (CD_3OD) δ=3.81 (s, 3H, CH_3O), 6.81—8.16 (m, 4H, Ar);

^{13}C NMR (CD$_3$OD) $\delta=55.9$ (CH$_3$O), 113.3, 131.6, 140.7, 163.5 (Ar), 213.8 (C=O); ^{77}Se NMR (CD$_3$OD) $\delta=350.9$. Found: C, 27.41; H, 1.91%. Calcd for $C_8H_7CsO_2Se$: C, 27.69; H, 2.03%.

Cesium 2-Chlorobenzenecarboselenoate (3h): Similarly to **3c**, the reaction of *O*-trimethylsilyl 2-chlorobenzenecarboselenoate (**1h**) (0.462 g, 1.58 mmol) with cesium fluoride (0.240 g, 1.58 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (3.5 mL) of methanol and ethanol gave 0.451 g (81%) of cesium 2-chlorobenzenecarboselenoate (**3h**) as yellow plates: Mp 155—170 °C (decomp); IR (KBr) 3047, 1584, 1524, (C=O), 1499, 1198, 1051, 1031, 956, 916, 767, 734, 701, 658, 637, 544, 469 cm^{-1}; ^{1}H NMR (CD$_3$OD) $\delta=7.20$—7.59 (m, Ar); ^{13}C NMR (CD$_3$OD) $\delta=127.1$, 128.9, 129.6, 129.8, 130.4, 151.2 (Ar), 216.8 (C=O); ^{77}Se NMR (CD$_3$OD) $\delta=517.1$. Found: C, 23.66; H, 1.14%. Calcd for $C_7H_4ClCsOSe$: C, 23.92; H, 1.15%.

Cesium 4-Chlorobenzenecarboselenoate (3i): Similarly to **3c**, the reaction of *O*-trimethylsilyl 4-chlorobenzenecarboselenoate (**1i**) (0.269 g, 0.92 mmol) with cesium fluoride (0.126 g, 0.92 mmol) in dichloromethane (5 mL) and recrystallization from a mixed solvent (3.5 mL) of methanol and ethanol (1 : 1) gave 0.222 g (76%) of cesium 4-chlorobenzenecarboselenoate (**3i**) as yellow needles: Mp 151—176 °C (decomp); IR (KBr) 3070, 1585, 1564, 1546 (C=O), 1482, 1396, 1281, 1195, 1153, 1100, 1084, 1011, 900, 838, 779, 738, 640, 625, 559, 474, 430 cm^{-1}; ^{1}H NMR (CD$_3$OD) $\delta=7.28$—8.12 (m, Ar); ^{13}C NMR (CD$_3$OD) $\delta=128.2$, 130.8, 132.1, 147.5 (Ar), 213.8 (C=O); ^{77}Se NMR (CD$_3$OD) $\delta=385.9$. Found: C, 23.66; H, 1.18%. Calcd for $C_7H_4ClCsOSe$: C, 23.92; H, 1.15%.

Potassium 4-Methylbenzenecarboselenoate (4e): Similarly to **3c**, the reaction of *O*-trimethylsilyl 4-methylbenzenecarboselenoate (**1e**) (0.320 g, 1.18 mmol) with potassium fluoride (0.069 g, 1.18 mmol) in dichloromethane (5 mL) for 45 h and recrystallization from a mixed solvent (10 mL) of methanol and ethanol (1 : 1) gave 0.126 g (45%) of potassium 4-methylbenzenecarboselenoate (**4e**) as yellow plates. The salt (**4e**) was converted into *Se*-methyl 4-methylbenzenecarboselenoate (91%). The IR spectrum was exactly consistent with that of the authentic sample.[3)]

(4e): Mp 128—153 °C (decomp); IR (KBr) 3050, 1612, 1583, 1535 (C=O), 1301, 1202, 1164, 1113, 904, 828, 798, 723, 685, 672, 474 cm^{-1}; ^{1}H NMR (CD$_3$OD) $\delta=2.30$ (s, 3H, CH$_3$), 7.09—8.07 (m, 4H, Ar); ^{13}C NMR (CD$_3$OD) $\delta=21.5$ (CH$_3$), 128.8, 129.4, 142.1, 145.0 (Ar), 215.3 (C=O); ^{77}Se NMR (CD$_3$OD) $\delta=351.8$.

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10) Towards oxygen, aromatic Rb and Cs salts appear to be more stable than the corresponding Li and Na salts.

11) The black solid formed by exposing $CH_3COSeCs$ under Ar atmosphere at room temperature showed no absorption band due to the organic moiety in IR spectrum.

12) For example, the signals of *Se*-methyl benzenecarboselenoate, 2-methyl- and 4-methoxy-benzenecarboselenoate were observed at $\delta=444.2$, $\delta=475.4$, and $\delta=428.7$ in ^{77}Se NMR Spectra, respectively.

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